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| <p>We are concentrating our efforts on the synthesis and characterization of molecularly dispersed polymer-ceramic nanocomposites and the development of new thermosets. The synthesis of the nanocomposites involves dispersion of an organically modified mica-type silicate (OMTS) in a suitable organic monomer, followed by polymerization. Under proper conditions delamination of the OMTS into individual silicate layers occurs, which ultimately become dispersed within the macromolecular matrix. This approach has a number of advantages over conventional processing of composites, such as 1) molecular dispersion of the silicate takes full advantage of the high aspect ratio (100-1000) particles, 2) functionalized organic molecules bound to the surface of the silicate can crosslink with the epoxy resin to enhance interfacial adhesion, and 3) enhanced physical properties can be achieved at low silicate loadings, resulting in lightweight composites. New liquid crystalline thermosets have been developed with superior fracture and modulus properties. They are also capable of orientation-on-demand behavior.</p> | | | |
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FINAL TECHNICAL REPORT

Grant Number:
F49620-92-J-0132

Molecularly Dispersed Polymer-Ceramic Nanocomposites

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Molecularly Dispersed Polymer-Ceramic Nanocomposites

Status of Effort:

We concentrated our efforts on the synthesis and characterization of molecularly dispersed polymer-ceramic nanocomposites and the development of new thermosets. The synthesis of the nanocomposites involves dispersion of an organically modified mica-type silicate (OMTS) in a suitable organic monomer, followed by polymerization. Under proper conditions delamination of the OMTS into individual silicate layers occurs, which ultimately become dispersed within the macromolecular matrix. This approach has a number of advantages over conventional processing of composites, such as 1) molecular dispersion of the silicate takes full advantage of the high aspect ratio (100-1000) particles, 2) functionalized organic molecules bound to the surface of the silicate can crosslink with the epoxy resin to enhance interfacial adhesion, and 3) enhanced physical properties can be achieved at low silicate loadings, resulting in lightweight composites. New liquid crystalline thermosets have been developed with superior fracture and modulus properties. They are also capable of orientation-on-demand behavior. This means tuned orientation can be achieved to control properties such as the coefficient of thermal expansion and moisture uptake. These new thermosets are suited to intercalation reactions.

Accomplishments/New Findings:

We were particularly interested in utilizing thermosetting polymers (e.g. epoxies) to synthesize novel composites that can be used in electronic packaging applications. In the past year, we have succeeded in preparing crosslinked epoxy networks containing 0-20% by weight mica-type silicate in which the silicate sheets are molecularly dispersed within the epoxy matrix. The composite resin can be mixed, applied in various forms (e.g. as adhesive films, coatings, or castings), and cured by conventional means. The resulting composite exhibits molecular dispersion of the silicate layers in the epoxy matrix, good optical clarity, and significantly improved dynamic mechanical properties compared to the unmodified epoxy.

A new polymer-ceramic nanocomposite has been synthesized consisting of well-dispersed, two-dimensional layers of an organically modified mica-type silicate (MTS) within a degradable poly(ϵ -caprolactone) matrix. A protonated amino acid derivative of MTS was used to promote delamination/dispersion of the host layers and initiate ring-opening polymerization of ϵ -caprolactone monomer, resulting in poly(ϵ -caprolactone) chains that are ionically bound to the silicate layers. The polymer chains can be released from the silicate surface by a reverse ion-exchange reaction and were shown to be spectroscopically similar to pure poly(ϵ -caprolactone). Thick films of the polymer nanocomposite exhibit a significant reduction in water vapor permeability that shows a linear dependence on silicate

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content. The permeability of nanocomposite containing as low as 4.8% silicate by volume was reduced by nearly an order of magnitude compared to pure poly(*e*-caprolactone).

An epoxy-silicate nanocomposite has been prepared by dispersing an organically modified mica-type silicate in an epoxy resin (diglycidyl ether of bisphenol-A, DGEBA) and curing in the presence of nadic methyl anhydride (NMA), benzylidimethylamine (BDMA), or boron trifluoride monoethylamine (BTFA) at 100-200 °C. Molecular dispersion of the layered silicate within the cross-linked epoxy matrix was verified using X-ray diffraction and transmission electron microscopy, revealing layer spacings of 100 Å or more and good wetting of the silicate surface by the epoxy matrix. The curing reaction appears to involve the hydroxyethyl groups of the alkylammonium ions located in the galleries of the organically modified silicate, which participate in the cross-linking reaction and result in direct attachment of the polymer network to the molecularly dispersed silicate layers. The nanocomposite exhibits a broadened T_g at slightly higher temperature than the unmodified epoxy. Furthermore, the dynamic storage modulus of the nanocomposite containing 4 vol-% silicate was approximately 58% higher in the glassy region and 450% higher in the rubbery plateau region compared to the unmodified epoxy.

In addition to the studies of intercalation and molecular dispersion of polymers with single silicate layers, we have been exploring liquid crystalline thermosets as self-organizing organic laminates. Crosslinked networks containing rigid-rod molecules have high thermal stability and good mechanical properties. Furthermore, thermosets based on low molar mass liquid crystalline precursors (such as dicyanate and diepoxy-compounds) were shown to frequently form a mesophase of a smectic type structure. Along with developing new high performance materials suitable for electronic packaging, this capability offers many exciting possibilities including a new route to preparing Langmuir-Blodgett-like bulk materials.

The attractive physical properties of cyanate ester resins make these materials an important class of high-performance polymer thermosets for applications such as electro-optic coatings and thin film dielectrics. Triazine networks have been used as insulating materials for over 25 years; however, in order to meet future requirements such materials must exhibit appropriate glass transition temperatures, high thermal stability, high moduli, good adhesion at elevated temperatures, low dielectric losses, and a low coefficient of thermal expansion (CTE). With our approach we are able to directly control their mechanical and physical properties by processing new liquid crystalline cyanate ester resins in electric fields. Combining new LC materials with non-LC cyanate monomers leads to a variety of novel ordered network structures and is a convenient method for modifying and controlling their chemical and physical

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properties. Studies of the new LC thermosets and their mixtures with non-LC materials will be described.

The techniques we are developing for producing oriented thin film structures might lead to membranes with unusual mechanical, separation, optical or even electrical properties. Our orientation process makes use of the dielectric anisotropy present in ester-based mesogenic groups. By applying AC fields of different frequencies while curing, we have been able to form networks with orientation-on-demand either in the plane of the film or perpendicular to the film plane.

The influence of the crosslinking reaction on the formation and development of a liquid crystalline (LC) phase in an LC thermoset was examined. Polarizing optical microscopy and X-ray diffraction at the Cornell High-Energy Synchrotron Source (CHESS) were used to provide information about the evolution of the microstructure in real time. By understanding the curing process, curing procedures that control the structural order in LC thermosets were developed.

Personnel

Phillip Messersmith, Postdoctoral Associate

Audrey Robinson, Graduate Student

Hilmar Körner, Postdoctoral Associate

Publications:

P.B. Messersmith and E.P. Giannelis, "Polymer-Layered Silicate Nanocomposite: In-Situ Intercalative Polymerization of n-caprolactone in Layered Silicates", *Chemistry of Materials*, 5, 1064, 1993.

R.A. Vaia, H. Ishii and E.P. Giannelis, "Synthesis and Properties of Two-Dimensional Polymer-Silicate Nanostructures by Direct Polymer Melt Intercalation", *Chemistry of Materials*, 5, 1694, 1993.

R.A. Vaia, R.K. Teukolsky and E.P. Giannelis, "Interlayer Structure and Molecular Environment of Alkyl Ammonium Layered Silicates", *Chemistry of Materials*, 6, 1017, 1994.

P.B. Messersmith and E.P. Giannelis, "Synthesis and Characterization of Layered Silicate-Epoxy Nanocomposites", *Chemistry of Materials*, 6, 1719, 1994.

P.B. Messersmith and E.P. Giannelis, "Synthesis and Barrier Properties of Poly(n-caprolactone)-Layered Silicate Nanocomposite", *Journal of Polymer Science A: Polymer Chemistry*, 33, 1047, 1995.

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P.B. Messersmith and E.P. Giannelis, "Synthesis, Characterization and Properties of Molecularly Dispersed Polymer-Silicate Nanocomposites" in *Novel Techniques in Synthesis and Properties of Advanced Materials*, J. Singh and S.M. Copley, Eds., in press.

E.P. Giannelis, "Organoceramic Nanocomposites", in Biomimetic Approaches in Materials Science, S. Mann, Ed., VCH, accepted.

E.P. Giannelis, "Polymer Layered Silicate Nanocomposites", *Advanced Materials*, submitted.

E.P. Giannelis, "Synthesis and Properties of Polymer-Layered Silicate Nanocomposites", *Japan Plastics*, submitted.

Ya. S. Freidzon, H. Zhong and C. K. Ober, "Thermosets Based On Mixtures Of Liquid Crystalline Polymers and Mesogenic Dicyanates", *Chem. Mater.*, under revision.

N. Johnen, H. K. Kim and C. K. Ober, "Polyphenylene Copolymers as Materials for Microelectronics", in H. Ito, S. Tagawa and K. Horie, ed., Polymeric Materials for Microelectronic Applications, *ACS Symposium Series 579*, American Chemical Society, Washington, DC 1994.

A. Shiota and C. K. Ober, "Synthesis and Curing of Novel LC Twin Epoxy Monomers for Liquid Crystal Thermosets", *J. Polym. Sci.: Polym. Chem. Ed.*, submitted.

N. A. Johnen, L. L. Beecroft and C. K. Ober, "Formation Of Transparent Silica-Polymer Hybrids Based On Siloxane-Containing Poly(Imides)", in J. Hedrick and J. Labadie, ed., Recent Advances in Step Growth Polymerization, *ACS Symposium Series xx*, American Chemical Society, Washington, DC 1995.

Interactions:

Talks by C. Ober:

Materials Research Society Meeting, San Francisco, CA, April 8-12, 1996.
"Orientation-on-Demand LC Networks", *invited talk*

American Chemical Society Meeting, Chicago, IL, August 20-24, 1995.
"Curing of Liquid Crystalline Networks in Electric Fields:
Preparation of Oriented Thin Films"

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Polymer Gordon Research Conference, Henneker, NH, June 25 - 30, 1994.
"Recent Developments in LC Thermosets", *invited talk*.

CHESS Annual Users Meeting, Ithaca, NY, June 20 - 21, 1995. "Synchrotron Studies of Liquid Crystal Monomers and Polymers: Orientation-on-Demand", *invited talk*

Intel Corp., Santa Clara, CA, March 3, 1995. "Imageable Polymers for 193 nm Resists and Low Dielectric Applications", *invited talk*.

Dow Chemical Co., Midland, MI, March 2, 1995. "New Developments in Liquid Crystalline Thermosets", *invited talk*.

Materials Research Society Meeting, Boston, MA, Nov. 28-30, 1994.
"The Synthesis, Structure and Properties of Liquid Crystalline Triazine Thermosets"

Talks by E. P. Giannelis:

Wright Patterson AFB (January 1994)
Cornell Univ., Dept. of Textiles (February 1994)
Michigan State University (March 1994)
MRS Spring Meeting (April 1994)
US-Japan Symposium on Inorganic-Organic Hybrids (May 1994)
AFOSR/ONR Workshop on Advanced Structural Materials (May 1994)
Fourth International Conference on Polymer Electrolytes (June 1994)
NSF Solid State Chemistry Tutorial (June 1994)
GORDON Research Conference on Solid State Ionics (June 1994)
GORDON Research Conference on High Performance Thermosets (July 1994)
8th International Symposium on Molecular Recognition, Ottawa, Canada (August 1994)
SRC Topical Conference on Low Dielectric Constant Materials, Troy, NY (August 1994)
MRS Fall Meeting, Boston, MA (November 1994)
UCSB, Santa Barbara, CA (February 1995)
Organic and Inorganic Polymer Workshop, Napa Valley, CA (1995)
UCLA, Los Angeles, CA (March 1995)
Princeton University, Princeton, NJ (March 1995)
University of Connecticut, Storrs, CT (April 1995)
Polymer Outreach Program, Short Course on Nanocomposites, Ithaca, NY (May 1995)
78th Canadian Society for Chemistry Conference, Guelph, ON (May 1995)
8th International Symposium on Intercalation Compounds, Vancouver, BC (May

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1995)

NSF, Solid State Chemistry Tutorial, Ithaca, NY (June 1995)

Access in Nanoporous Materials Symposium, E. Lansing, MI (June 1995)

Gordon Conference on Layered and Zeolitic Materials (June 1995)

Gordon Conference on Polymers (June 1995)

NRC Democritos, Athens, Greece (July 1995)

Polymer Battery Workshop, WPAFB (August 1995)

New Discoveries: none

Honors: (C. Ober) Humboldt Research Fellow and Guest Professor, Max-Planck-Institut für Polymerforschung, Mainz, Germany.